

---

(12) UK Patent Application (19) GB (11) 2 071 708 A

---

- (21) Application No 8105343
- (22) Date of filing 20 Feb 1981  
Date lodged 20 Feb 1981
- (30) Priority data
- (31) 8008597
- (32) 13 Mar 1980
- (31) 8014139
- (32) 29 Apr 1980
- (33) United Kingdom (GB)
- (43) Application published  
23 Sep 1981
- (51) INT CL<sup>3</sup>  
D06P 5/00 5/12
- (52) Domestic classification  
D1B 2J 2L29A 2L29C  
2L34B 2L3
- (56) Documents cited  
None
- (58) Field of search  
D1B
- (60) Derived from Application  
No 8105342 under Section  
15(4) of the Patents Act  
1977
- (71) Applicant  
Imperial Chemical  
Industries Limited,  
Imperial Chemical  
House, Millbank,  
London SW1P 3JF
- (72) Inventor  
John Reginald Provost
- (74) Agent  
Peter Frederick Clark,  
Imperial Chemical  
Industries Limited, Legal  
Department: Patents,  
Thames House North,  
Millbank, London SW1P  
4QG

(54) Textile Printing Process

(57) A "wet-on-wet" process for the resist or discharge printing of synthetic textile materials uses alkali-dischargeable disperse dyestuffs which are free from sulphonic acid and carboxylic acid groups, and free

from carboxylic acid ester groups which if hydrolysed would leave carboxylic acid groups attached to the dyestuff molecule, and using sodium or potassium silicate as the alkali. The prints have much better definition than when conventional alkalies are used.

GB 2 071 708 A

## SPECIFICATION

### Textile Printing Process

This invention relates to an improved process for the resist or discharge printing of synthetic textile materials.

5 Resist printing is a method of textile printing in which an undyed textile material is first printed with a substance (the resist) which prevents the uptake or fixation of a subsequently applied dyestuff, so that there is obtained a white pattern on a coloured ground, or a pattern of contrasting colour to the ground by incorporating suitable dyestuffs or colour-producing substances in the resist print paste.

10 Discharge printing is a method of textile printing in which dyed textile material is printed with a chemical composition (the discharge) that destroys the dyestuff locally to give a white pattern, or in which a second dyestuff, applied simultaneously with the discharge, produces a pattern of contrasting colour.

15 United Kingdom Patent Specification No. 1543724 described and claims a process for producing discharge printing effects in a coloured ground shade on a synthetic textile material, which comprises applying to that area of the material where the ground shade and the discharge effect are wanted one or more disperse dyes which contain at least one carboxylic ester group but are free from carboxylic acid and sulphonic acid groups, and in a separate stage applying to the material where the discharge effect is wanted a printing paste which is alkaline or becomes alkaline on heating or steaming and which does not contain any reducing agent, thereafter heating or steaming the material and thereafter washing the material.

20 The above process is typically carried out in the following 7 stages in which the textile material is:—

1. Printed with an alkaline print paste.
2. Dried.
- 25 3. Padded with the disperse dyestuff.
4. Dried.
5. Heat treated or steamed.
6. Washed.
7. Dried.

30 Alternatively, stages 1 and 3 can be reversed, so that the dyestuff is applied to the textile material before the alkaline print paste.

During stage 5, in which the textile material is subjected to the action of heat or steam, the disperse dyestuff in contact with the alkali is converted into a water-soluble form, whilst the disperse dyestuff which is not in contact with the alkali is fixed on the textile material. The water-soluble form of the dyestuff is then removed from the textile material by the washing treatment of stage 6.

35 It would be desirable if, in the above process, the first drying operation (stage 2) could be eliminated so that stage 1 is followed immediately by stage 3. This "wet-on-wet" process would have the advantages that the process has one stage less, with consequent saving in drying plant occupation time, and also the saving in the energy used to effect drying.

40 However, using printing pastes containing the alkaline agents which are normally employed, i.e. sodium hydroxide, sodium carbonate, sodium bicarbonate or potassium carbonate, it is found that the "wet-on-wet" technique gives prints having poor definition, because the alkali bleeds out of the print paste during the subsequent drying and fixation stages to give an unsightly dull white halo at the boundary between the originally applied alkaline resist and the subsequently applied dyestuff. This effect is known as "haloing", and prints which exhibit it are not commercially acceptable.

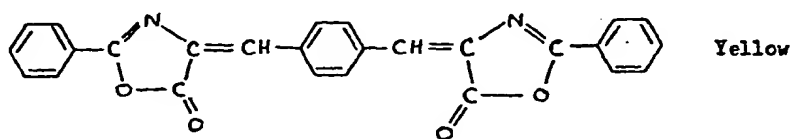
45 It has now been found that wet-on-wet resist or discharge prints having sharp definition between the different coloured areas of the print can be obtained if the alkali used in the print paste is sodium or potassium silicate.

According to the present invention there is provided a process for producing resist or discharge printing effects on a synthetic textile material which comprises applying to the textile material, in either order and without drying the textile material between the applications, (i) an alkaline printing paste containing sodium or potassium silicate, and which may contain one or more disperse dyestuffs free from sulphonic acid, carboxylic acid and carboxylic acid ester groups, the said dyestuffs being unaffected by alkali at the concentration present, and (ii) a printing paste or padding liquor containing at least one alkali dischargeable disperse dyestuff free from sulphonic acid and carboxylic acid groups and free from carboxylic acid ester groups which if hydrolysed would leave carboxylic acid groups attached to the dyestuff molecule, thereafter heating or steaming the material and thereafter washing the material.

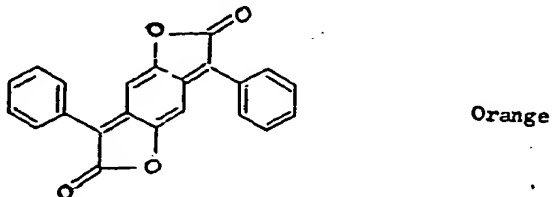
60 The alkali-dischargeable dyestuffs which are used in the process according to the present invention may be broadly classified as follows:—

A. Dyestuffs which contain one or more lactone rings which open in the presence of alkali with formation of the water-soluble alkali metal salts of the corresponding hydroxy carboxylic acid. Opening of the lactone ring may be accompanied by destruction of the chromophoric system of the dyestuff.

Examples of this class are the dyestuff of the formula:

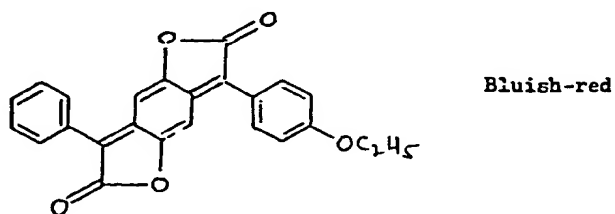
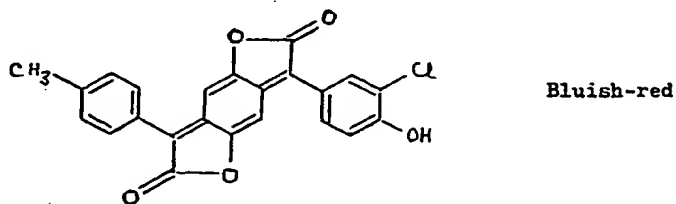
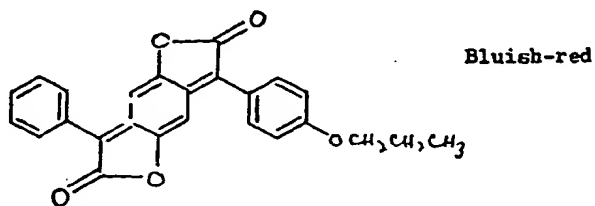
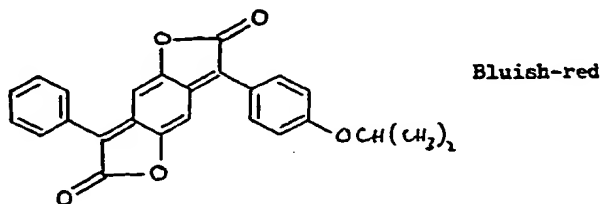


which is disclosed in German Offenlegungsschrift 2440405, and the dyestuff of formula:



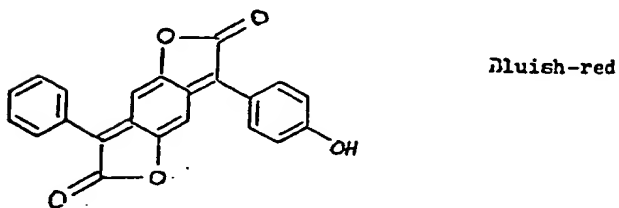
- 5 which is disclosed in UK Patent Specification No. 1568231.  
Also in this general class are the dyestuffs of the formulae:

5

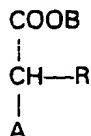


10

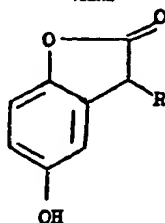
10



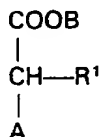
These unsymmetrically substituted compounds having the above-disclosed formulae may be obtained by reaction of equimolar quantities of hydroquinone and a compound of formula:



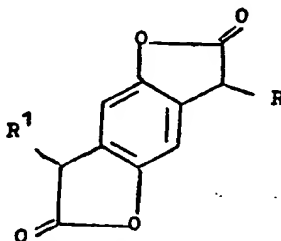
wherein A is hydroxyl, O-acyl or halogen; B is hydrogen, lower alkyl or aryl and R is phenyl which may carry one or more substituents, for example, lower alkyl, lower alkoxy, hydroxy, chlorine or bromine. In this specification the term "lower alkyl" and "lower alkoxy" mean alkyl and alkoxy groups respectively which contain 1 to 4 carbon atoms. The reaction may be carried out either in the absence of a solvent or in the presence of a high boiling solvent such as di- or tri-chlorobenzene to give the intermediate of formula:



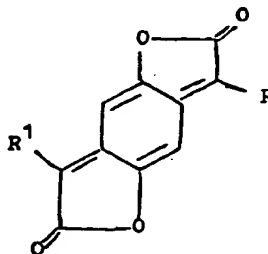
which is subsequently reacted with a compound of formula:



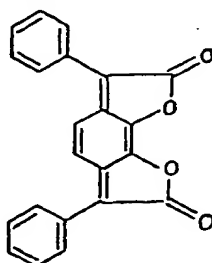
wherein A and B have the previously defined meanings and R<sup>1</sup> is phenyl which may carry one or more substituents, R<sup>1</sup> being different to R, to give a compound of formula:



which is then oxidised, preferably *in situ* by using nitrobenzene as reaction solvent or by treatment with an oxidising agent such as hydrogen peroxide in acetic acid, to give the desired dyestuff of formula:



There may also be used in the process of the present invention the dyestuff of formula:

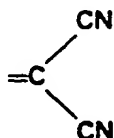


Orange

which is disclosed in European Patent Publication No. 23080.

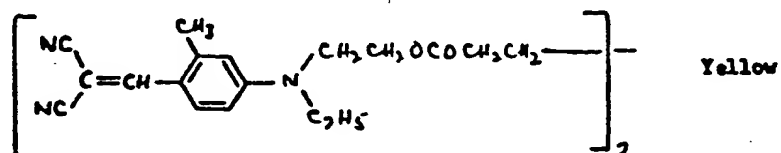
Other dyestuffs in class A which may be used in the present process are those which contain the umarin ring system.

**B. Methine dyestuffs containing at least one**

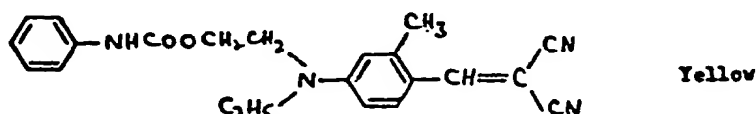


5 group, for example the dyestuff of formula:

5



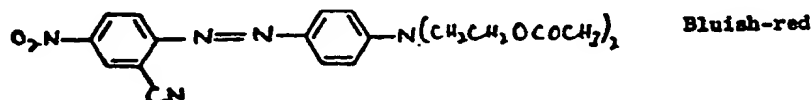
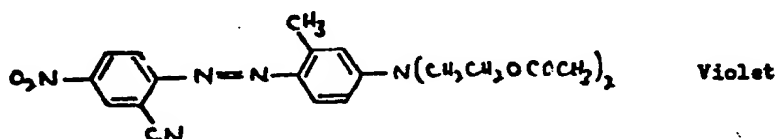
which is disposed in French Patent Specification No. 1551030, and the dyestuff of formula:



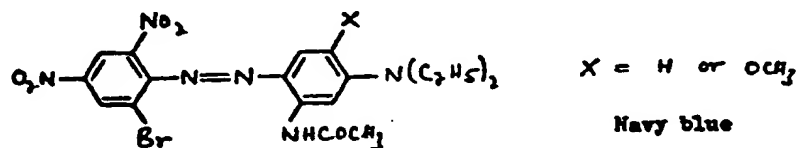
which is disclosed in US Patent Specification No. 2850520.

10 **C. Azo dyestuffs derived from anilines having at least two electron-withdrawing groups ortho and/or para to the amino group as diazo components and para-coupling amine coupling components, for example**

10



15

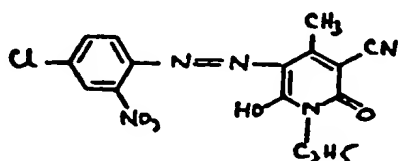


15

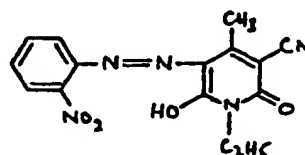
the first two of which are disclosed in UK Patent Specification No. 852493, and the last in UK Patent Specification No. 1050675.

20 **D. Dyestuffs containing groups which are capable of water-soluble salt formation in the presence of strong alkali, including azopyridone dyestuffs and dyestuffs containing phenolic hydroxyl groups or primary or secondary sulphonamide groups, for example:**

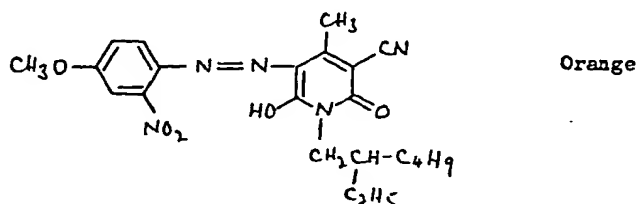
20



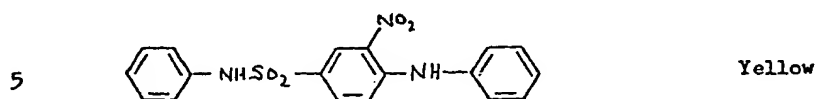
and



both of which are disclosed in UK Patent Specification No. 1256093; the dyestuff of formula:



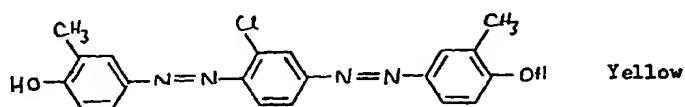
which is disclosed in UK Patent Specification No. 1398741; the dyestuff of formula:



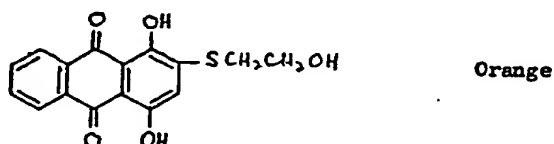
which is C.I. Disperse Yellow 42;  
the dyestuff of formula:

5

5

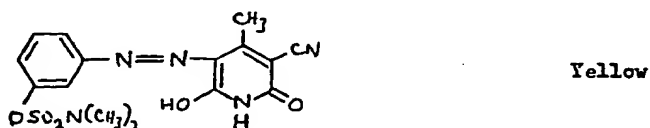
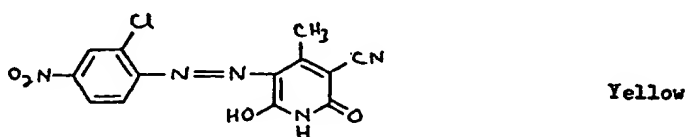


which is disclosed in UK Patent Specification No. 1016246;  
the anthraquinone dyestuff of formula:



10 which is disclosed in French Patent Specification No. 1371626, and the pyridone dyestuffs of formulae:

10

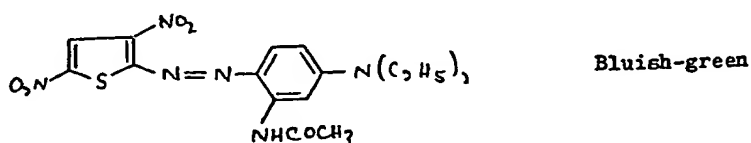
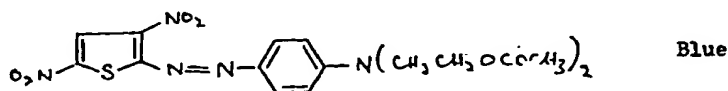


both of which are disclosed in UK Patent Specification No. 1095829.

15

E. Dyestuffs derived from 2-aminothiophenes as diazo components and para-coupling amines as coupling components, the thiophene nucleus being substituted by at least two electron-withdrawing groups, for example:

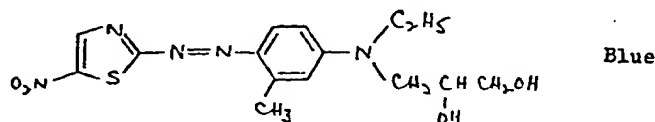
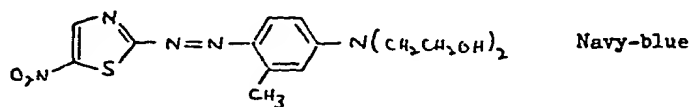
15



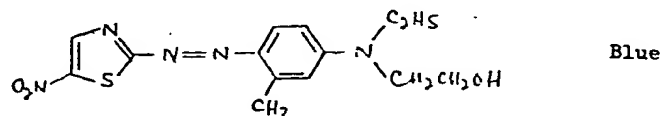
20 these dyestuffs being disclosed in UK Patent Specification Nos. 1394367 and 1394368, respectively.

20

F. Azo dyestuffs derived from 2-amino-5-nitrothiazole as diazo component and a para-coupling amine as coupling component, for example the dyestuffs of formulae:

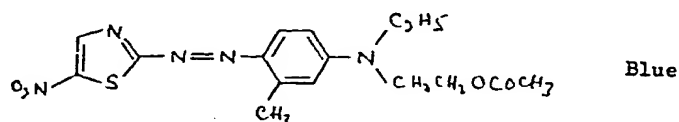


5



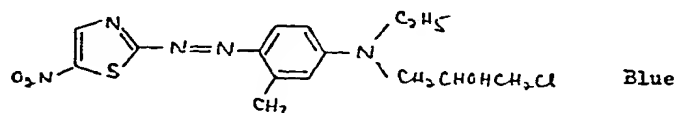
5

which are all disclosed in UK Patent Specification No. 723933;  
the dyestuff of formula:



which is disclosed in US Patent Specification No. 2790791, and the dyestuff of formula:

10



10

which is disclosed in UK Patent Specification No. 840903.

Also usable in the process and having excellent alkaline discharge properties are the miscellaneous dyestuffs C.I. Disperse Violet 88, C.I. Disperse Yellow 180, C.I. Disperse Violet 48, C.I. Disperse Blue 92, C.I. Disperse Yellow 93, C.I. Disperse Yellow 201, C.I. Disperse Yellow 88, C.I. Disperse Yellow 210, C.I. Disperse Red 203 and C.I. Disperse Yellow 202.

15

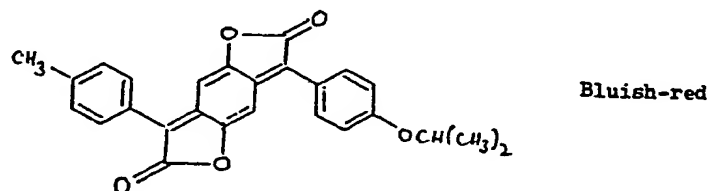
15

Other dyestuffs which may be used in the present process are those which discharge only partially (i.e. do not give a white discharge) and which do not leave a weak enough stain to allow all shades of illumination to be used, but which do show an even residual shade that allows the use of such dyestuffs for limited illuminated shades and which may be used for shading purposes.

20

20

Examples of such dyestuffs are (with reference to the previously defined classes):  
In class A:



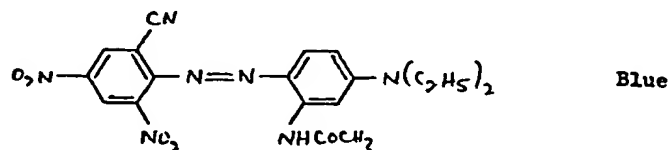
which may be prepared as described previously for similar dyestuffs in Class A.

In Class C:

The dyestuff of formula:

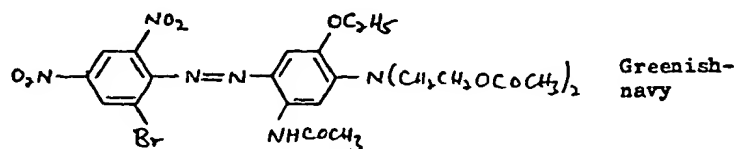
25

25



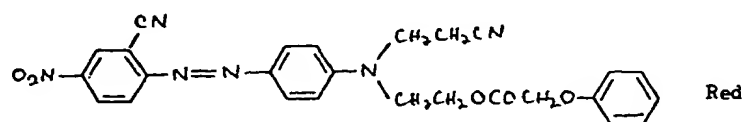
which is disclosed in UK Patent Specification No. 1080480.

The dyestuff of formula:



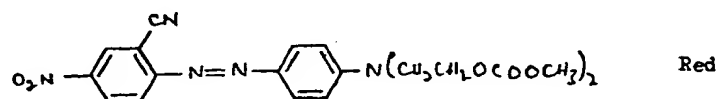
which is disclosed in UK Patent Specification No. 952468.

The dyestuff of formula:



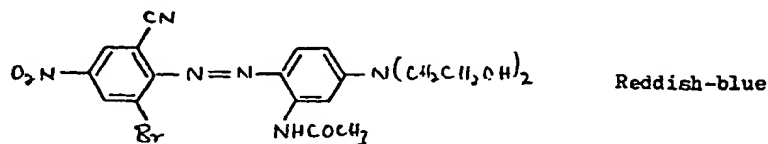
which is disclosed in UK Patent Specification No. 1225221.

The dyestuff of formula:



which is disclosed in French Patent Specification No. 1264090;

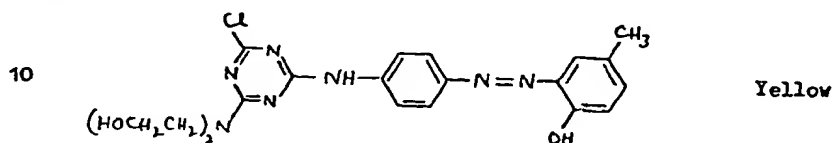
and the dyestuff of formula:



which is disclosed in UK Patent Specification No. 1140214.

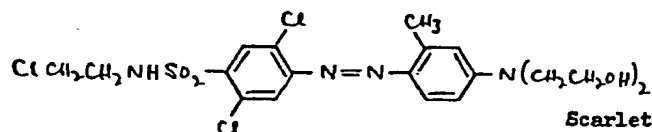
In Class D:

The dyestuff of formula:



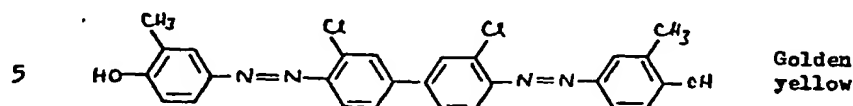
which is disclosed in UK Patent Specification No. 825377;

the dyestuff of formula:



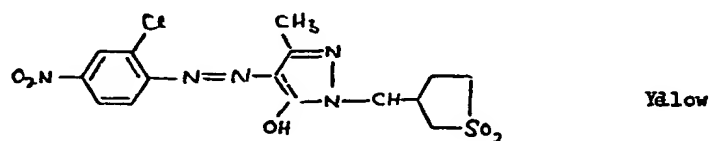
which is disclosed in UK Patent Specification No. 862269;

the dyestuff of formula:



which is disclosed in UK Patent Specification No. 1020303;

the dyestuff of formula:

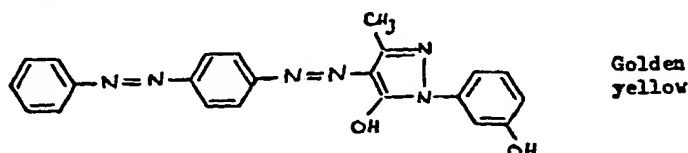


25 which is disclosed in UK Patent Specification No. 847181;

25

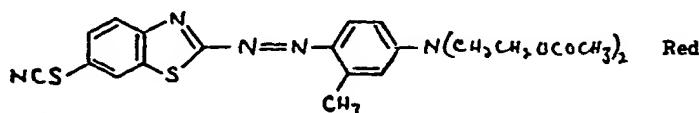


and the dyestuff of formula

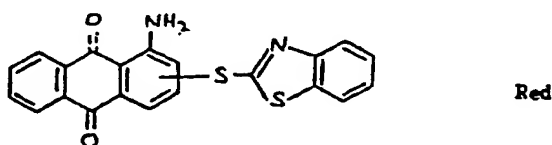


which is disclosed in UK Patent Specification No. 1171803.

Also included in the group of partially dischargeable dyestuffs are the miscellaneous dyestuffs of formulae:



which is disclosed in UK Patent Specification No. 859899, and



which is disclosed in UK Patent Specification No. 1027968, together with C.I. Disperse Red 72, C.I. Disperse Blue 139, C.I. Disperse Orange 55, C.I. Disperse Red 329 and C.I. Disperse Violet 40.

Any dyestuff which undergoes chromophore destruction in the presence of alkali to an extent such as to make it suitable for a ground shade in discharge printing may be used in the present process.

The sodium silicate which is used in the above process may be any of those grades of sodium silicate which are commercially available and is preferably a sodium silicate in which the molecular ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  is from 1.65:1.0 to 4.0:1.0. The potassium silicate which is used preferably has a molecular ratio of  $\text{SiO}_2$  to  $\text{K}_2\text{O}$  of from 2.0:1 to 4.0:1.

The amount of sodium or potassium silicate which is used in the printing paste (i) must provide sufficient alkali to discharge the disperse dyestuff in the padding liquor or printing paste (ii), and may be from 50 to 300 parts by weight per 1000 parts by weight of printing paste.

It is found that a sodium or potassium silicate having a high molecular ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  can be replaced in the printing paste by a smaller quantity of sodium or potassium silicate having a lower molecular ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ , without affecting the result.

The printing paste containing the sodium or potassium silicate must also contain a humectant such as ethylene glycol urea or, preferably, glycerol, a dye solvent such as polyethylene glycol, for example, a polyethylene glycol having a molecular weight in the region of 300, and a thickening agent. The latter must be stable to the other ingredients of the paste, and examples of suitable thickeners are starch derivatives such as starch ethers, carob-seed gum ethers, modified carboxymethylcelluloses and combinations of these, optionally in admixture with a water-in-oil or oil-in-water emulsion.

The padding liquor or print paste used to apply the alkali-dischargeable disperse dyestuff should also contain a carboxylic acid, for example, citric acid, to prevent premature interaction of the dyestuff with the alkaline sodium or potassium silicate, and a thickener such as one of those thickeners already mentioned above. There may also be present any of those adjuvants which are conventionally employed in the application of disperse dyestuffs to synthetic textile materials from such media, for example, carriers, fixation assistants, level dyeing assistants, dispersing agents and antifoam agents.

The heat treatment to which the textile material is subjected after the application of the print paste containing the sodium or potassium silicate and the print paste or padding liquor containing the disperse dyestuff can comprise a heat treatment for a short period at temperatures from  $150^\circ$  to  $220^\circ\text{C}$ . It is, however, preferred to subject the textile material to a steaming treatment, for example, saturated steam at  $100^\circ\text{C}$  for a few minutes followed by a dry heat treatment at  $160^\circ$  to  $220^\circ\text{C}$  or superheated steam at  $150^\circ$  to  $200^\circ\text{C}$ , or the use of saturated steam under pressure at  $115^\circ$  to  $150^\circ\text{C}$ .

The final washing stage of the process is conveniently carried out in the following sequence:—

(i) Cold water rinse.

(ii) Treatment in an aqueous alkaline bath at a pH above 8.0 and at a temperature from  $50^\circ$  to  $85^\circ\text{C}$ .

(iii) Rinse in water at  $60^\circ\text{C}$ .

(iv) Treatment in an aqueous bath containing 0.2% of sodium hydroxide and 0.2% of sodium hydrosulphite at  $60^\circ\text{C}$ .

(v) Treatment in an aqueous solution containing 0.2% of a non-ionic detergent at  $60^\circ\text{C}$ .

(vi) Cold water rinse.

after which the textile material is dried.

The synthetic textile materials used in the process of the invention can be in the form of non-woven fabric, felt, woven or knitted goods, or carpets. As examples of synthetic textile materials there may be mentioned secondary cellulose acetate and cellulose triacetate, polypropylene, acrylic, polyamide, and preferably aromatic polyester textile materials. If desired, the synthetic textile material can be in the form of a blend or union with a cellulose textile material, for example a polyethyleneterephthalate/cotton blend or union. In the case of such blends or unions the alkali-dischargeable disperse dyestuff can be used together with a reactive dye whose reactive groups, such as sulphatoethylsulphone groups, form a dye-fibre bond with the hydroxyl groups of the cellulose textile material which is hydrolysed under the alkaline conditions in those areas where the alkaline print paste is applied, or a reactive dyestuff containing one or more phosphonic acid groups which does not fix on cellulose in the presence of alkali.

The disperse dyestuff or dyestuffs which are optionally used in the alkaline printing paste containing sodium or potassium silicate can be any of the disperse dyestuffs not adversely affected by alkali which are conventionally employed in colouring synthetic textile materials. Examples of such dyestuffs are given in, for example, the Third Edition of the Colour Index which was published in 1971.

The invention is illustrated by the following Examples in which parts and percentages are by weight.

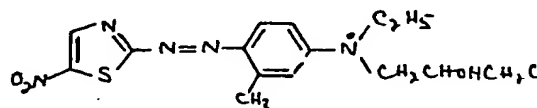
#### Example 1

A resist print paste comprising:

20	Glycerol	80 parts	20
	Polyethylene glycol (molecular weight 300)	80 parts	
	Sodium silicate (mol ratio $\text{SiO}_2:\text{Na}_2\text{O}=2.05:1.0$ )	160 parts	
	Solvitose C5 (12% solution; starch ether)	570 parts	
	Water	110 parts	
25		<hr/> 1000 parts	25

is printed on to a woven polyethylene terephthalate textile material, and without drying the textile material is then coated over all, including that part which has already been printed with the above resist paste, with the following print paste comprising:

Dyestuff of the formula:

30		10.00 parts	30
	Glycerol	22.80 parts	
	Citric acid	5.00 parts	
	Calgon PT (sequestering agent)	6.25	
	Sodium m-nitrobenzenesulphonate	30.00 parts	
35	Manutex F powder (sodium alginate thickener)	50.00 parts	35
	Water to	1000 parts	

The textile material is then dried on drying cylinders for 2 minutes at approximately 95°C, high temperature steamed at 170°C, for 8 minutes, washed off using the six-stage washing sequence described above and finally dried.

The resulting blue on white pattern has excellent definition. 40

If the above procedure is repeated using sodium carbonate, sodium hydroxide or potassium carbonate in place of sodium silicate the resulting prints have poor definition, bleeding-out of the alkali producing an unacceptable dull white halo round the edge of the blue areas of the print.

If the sodium silicate used in the above example is replaced by the same amount of a sodium silicate in which the molecular ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  is 1.65:1.0 a similar result is obtained; the amount of this latter sodium silicate can also be reduced to 100 parts without adverse effect on the sharpness of the resulting print. 45

Instead of the white resist print paste used in the first stage of this Example there is used a similar print paste containing, in addition to the ingredients specified above, one of the following disperse dyestuffs which are not sensitive to alkali: C.I. Disperse Yellow 63, C.I. Disperse Orange 96, C.I. Disperse Red 91, C.I. Disperse Red 210, C.I. Disperse Red 303, C.I. Disperse Blue 185, C.I. Disperse Blue 83, C.I. Disperse Red 11, C.I. Disperse Blue 95 and C.I. Disperse Violet 26. In each case there is obtained a final print having the appropriately coloured pattern on a blue ground shade. The prints have excellent definition with no haloing effect, no bleeding of the illuminant dyestuff and with bright illuminant shades. 50

The words "Calgon", "Manutex" and "Solvitose" are Registered Trade Marks. 55

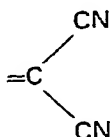
**Example 2**

The procedure is repeated except that the dyestuff used in the second print paste is replaced by an equal weight of any one of the other dyestuffs hereinbefore specifically identified.

In each case there is obtained a pattern having excellent definition between the discharged and undischarged areas of the print.

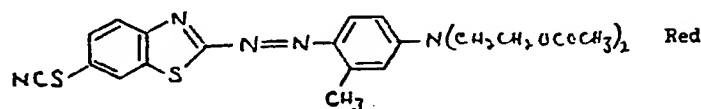
**Claims**

1. A process for producing resist or discharge printing effects on a synthetic textile material which comprises applying to the textile material, in either order and without drying the textile material between the applications, (i) an alkaline printing paste containing sodium or potassium silicate, and which may contain one or more disperse dyestuffs free from sulphononic acid, carboxylic acid and carboxylic acid ester groups, the said dyestuffs being unaffected by alkali at the concentration present, and (ii) a printing paste or padding liquor containing at least one alkali dischargeable disperse dyestuff free from sulphononic acid and carboxylic acid groups, and free from carboxylic acid ester groups which if hydrolysed would leave free carboxylic acid groups attached to the dyestuff molecule, thereafter heating or steaming the material and thereafter washing the material.
2. A process as claimed in claim 1 wherein the alkali-dischargeable disperse dyestuff is selected from one of the following classes:
  - A. Dyestuffs which contain one or more lactone rings which open in the presence of alkali with formation of the water-soluble alkali metal salt of the corresponding hydroxy carboxylic acid.
  - B. Methine dyestuffs containing at least one

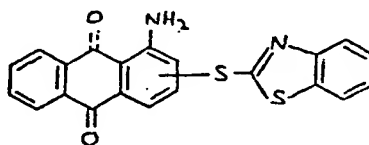


group.

- C. Azo dyestuffs derived from anilines having at least two electron-withdrawing groups ortho and/or para to the amino group as diazo components and para-coupling amine coupling components.
- D. Dyestuffs containing groups which are capable of water-soluble salt formation in the presence of strong alkali.
- E. Azo dyestuffs derived from 2-aminothiophenes as diazo components and para-coupling amines as coupling components, the thiophene nucleus being substituted by at least two electron-withdrawing groups.
- F. Azo dyestuffs derived from 2-amino-5-nitrothiazole as diazo component and a para-coupling amine as coupling component.
- G. Miscellaneous dyestuffs selected from the dyestuff having the formula:



the dyestuff having the formula:



and C.I. Disperse Violet 88, C.I. Disperse Yellow 180, C.I. Disperse Violet 48, C.I. Disperse Blue 92, C.I. Disperse Yellow 93, C.I. Disperse Yellow 201, C.I. Disperse Yellow 88, C.I. Disperse Yellow 210, C.I. Disperse Red 203, C.I. Disperse Yellow 202, C.I. Disperse Red 72, C.I. Disperse Blue 139, C.I. Disperse Orange 55, C.I. Disperse Red 329 and C.I. Disperse Violet 40.

3. A process as claimed in claim 1 or claim 2 wherein the sodium silicate has a molecular ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  from 1.65:1.0 to 4.0:1.0, and the potassium silicate has a molecular ratio of  $\text{SiO}_2$  to  $\text{K}_2\text{O}$  from 2.0:1.0 to 4.0:1.0.
4. A process as claimed in any one of claims 1 to 3 wherein the printing paste containing the sodium or potassium silicate also contains a humectant and a thickening agent.

5. A process as claimed in any one of claims 1 to 4 wherein the printing paste containing the sodium or potassium silicate also contains a dye solvent.

6. A process as claimed in claim 1 substantially as hereinbefore described in either of the foregoing Examples.

5 7. Synthetic textile materials whenever resist or discharge printed by means of a process as claimed in any one of the preceding claims. 5

---

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981. Published by the Patent Office,  
25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.